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INTERIM REPORT

EFFECT OF WATER ON HYDRAULIC BRAKE FLUID

BY

CHARLES B. JORDAN

MAY 1966

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U. S. ARMY COATING & CHEMICAL LABORATORY

Aberdeen Proving Ground
Maryland

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CCL REPORT NO. 198

INTERIM REPORT

EFFECT OF WATER ON HYDRAULIC BRAKE FLUID

BY

CHARLES B. JORDAN

MAY 1966

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DEPARTMENT OF THE ARMY PROJECT NO.
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U.S. ARMY COATING AND CHEMICAL LABORATORY
ABERDEEN PROVING GROUND
MARYLAND

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ABSTRACT

The object of this study was to determine the effect of absorbed moisture on the physical and chemical characteristics of polar type hydraulic brake fluids. Specific studies were carried out on the effect of moisture on equilibrium boiling point, flash point, cold temperature viscosity, oxidation stability, and effect on rubber with several polar brake fluids of varying chemical composition.

Moisture produced the following effects - a. Boiling points are lowered in all brake fluids - drastically in so-called "high boiling" fluids. b. Flash points are increased. c. Cold temperature viscosities are usually increased. d. The stability of the brake fluid toward oxidation is decreased. e. Rubber swelling and softening is decreased.

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I. INTRODUCTION

The U. S. Army Coating and Chemical Laboratory, Aberdeen Proving Ground, Maryland was authorized by AMC Directive, AMCMS Code 5025.11.802, dated 24 July 1964 to conduct research on hydraulic brake fluids. Much publicity has been given to the problem of moisture entering vehicle brake systems through absorption. This report contains data showing the effect of moisture on different physical and chemical properties of polar type brake fluids.

II. DETAILS OF TEST

A. Water in Brake Fluid from Vehicles in Operation - Brake fluid was removed from the master cylinders of 35 military vehicles and 9 civilian vehicles, selected at random at Aberdeen Proving Ground, Maryland. No previous vehicle history was available. Equilibrium boiling points were conducted according to the procedure outlined in Federal Specification VV-B-680. The amount of water was determined by the Karl Fischer Method (7).

B. Effect of Water on Boiling Point of Brake Fluids - Ten brake fluids were selected representing fluids currently being used in military and civilian vehicles. Three of these fluids met Federal Specification VV-B-680, two fluids met Military Specification MIL-H-13910A, and two fluids met Military Specification MIL-P-46046A, and three were high boiling fluids meeting SAE Specification J70b - 70R3.

The original equilibrium boiling points were determined by the procedure outlined in Federal Specification VV-B-680 and water content of each fluid was determined by the Karl Fischer Method (7). Water was added in 1% increments and equilibrium boiling points were determined after each addition.

C. Effect of Water on -40°F. Viscosity of Brake Fluids - Viscosity of thirteen brake fluids were determined at -40°F. with and without 2% water added. Included were twelve fluids meeting Federal Specification VV-B-680 and one fluid meeting Military Specification MIL-H-13910A. Several of the fluids were then exposed to a 65% relative humidity at 80°F. for a period of 7 days. Water determinations were made by the Karl Fischer Method (7) and -40°F. viscosities were taken.

D. Effect of Water on Flash Point of Brake Fluids - Flash points were conducted on four brake fluids by the procedure outlined in paragraph 4.5.2 of Federal Specification VV-B-680. Included were three fluids meeting Federal Specification VV-B-680 and one fluid meeting Military Specification MIL-H-13910A. Water was added to the fluids in 2% increments and flash points were determined after each addition.

E. Effect of Water on Oxidation Stability of Brake Fluids - Twelve brake fluids meeting Federal Specification VV-B-680 were subjected to the oxidation stability test outlined in paragraph 4.5.14 of Federal Specification VV-B-680 except that in one test 0.5% Benzoyl Peroxide was added to the brake fluid and in the second test 0.5% Benzoyl Peroxide and 5% water was added. In the specification test, only 0.2% Benzoyl is added. The excess peroxide decreased the stability to borderline values so that the effect of water would be more evident and more pronounced. The test specimens were visually examined for evidence of corrosion (pitting, etching, discoloration) after ten days storage at 158°F.

F. Effect of Water on Rubber Swelling and Softening - Rubber swelling and durometer hardness change was determined on ten brake fluids meeting Federal Specification VV-B-680 according to the procedure outlined in paragraph 4.5.10 with and without 5% water added. Cups meeting MIL-C-14055B were used in this test.

III. RESULTS OF TESTS

A. Water in Brake Fluids from Vehicles in Operation - Boiling points and percent water are contained in Table I. It will be noted that the fluids from the military vehicles have picked up water in amounts ranging up to 4.85% with the average pickup on the 35 vehicles being 2.40%. The civilian vehicles have picked up an average of 1.37% water. Boiling points on the military vehicles range as low as 246°F. with 69% of the fluids boiling below the minimum requirements specified in Federal Specification VV-B-680. The new vehicles containing diaphragms did not accumulate as much water as the other vehicles. However, there are indications that eventually the brake fluid in these vehicles will pick up enough water to lower the boiling points into the critical ranges.

B. Effect of Water on Boiling Point of Brake Fluids - Table II shows the effect of water on the boiling points of the brake fluids. Small percentages of water drastically reduce the boiling points of high boiling fluids. An excellent example is where 1% of water lowers the boiling point of a brake fluid from 558°F. to 384°F., a drop of 174°. A fluid which originally boils at 322°F. only drops 16°F., upon the addition of 1% water. Six or seven percent water brings the boiling points of all brake fluids tested to the same value of 240° to 250°F.

C. Effect of Water on -40°F. Viscosity of Brake Fluids - As can be seen in Table III, water increased the sub-zero temperature viscosity of nine of the brake fluids. Fluids such as No. 11 which originally have viscosities approaching the maximum allowable range would not meet specification requirements after water pick-up.

D. Effect of Water on Flash Point of Brake Fluids - Table IV shows that water increases the flash point of brake fluids. The azeotropes formed between water and the brake fluid solvents flash at higher temperatures than the solvents alone.

E. Effect of Water on Oxidation Stability of Brake Fluids - Water greatly reduces the oxidation stability of brake fluids, as shown in Table V. In the tests recorded in Table V, the level of Benzoyl Peroxide was raised to the point where one of twelve brake fluids exhibited excessive corrosion of test specimens. Several of the other fluids were borderline. With added water, three fluids showed excessive corrosion of test specimens and nine of the twelve fluids showed increased corrosion over the tests without water.

F. Effect of Water on Rubber Swelling and Softening - Table VI shows that the addition of 5% water reduced the amount of rubber swelling and softening in every test.

IV. DISCUSSION

The deleterious effect of water is getting much publicity in all committees dealing with brake fluids both in the Government and in industry. Modern brake system designers are attempting to overcome the problem of water pickup by certain mechanical means, such as diaphragms in the master cylinders and more efficient boots in the wheel cylinders. These devices slow down the water accumulation in the system but do not eliminate it, so that in a matter of time, water will be absorbed.

If the frequency rate of low boiling brake fluid found in the present study conducted at Aberdeen Proving Ground is representative of that which is in all military vehicles, a very real problem exists and definite measures should be taken to alleviate it. Sixty-nine per cent of the vehicles screened at Aberdeen Proving Ground contained brake fluid in the master cylinders which boil below minimum standards. One source of information reported that fluid in the wheel cylinders accumulates water more rapidly than fluid in the master cylinders. This means that the percentage of bad fluid is higher than 69% and the problem is even more critical, since highest temperatures are recorded in the areas surrounding the wheel cylinders and low boiling fluids are much more apt to vaporize.

Although the problem of low temperature viscosity is not as critical as boiling point, difficulties can be expected in our northern states during cold weather. Brakes of vehicles subjected to periods of "cold-soaking" will not operate properly if viscosities exceed the maximum values listed in the specifications. Power transmission and release is too slow.

The problem of brake fluid stability is also becoming increasingly evident. During the past few years large numbers of reports have been filed concerning gumming and corrosion of brake parts in military vehicles. This report shows that the chemical breakdown of the brake fluid is accelerated by the presence of water and studies toward the solution of this specific area of difficulty should continue.

V. RECOMMENDATIONS

The following possible phases of action should be considered:

A. The trend in brake design should continue toward devices which eliminate or cut down the exposure of fluid to atmosphere and water absorption.

B. Brake fluid formulation development should be directed toward the use of less hygroscopic chemicals. Development of improved stabilizing inhibitors should continue.

C. Brake system maintenance should be more frequent and more thorough.

VI. REFERENCES

1. Authority: AMC Directive, AMCMS Code 5025.11.802 dated 24 July 1964.
2. Federal Specification VV-B-680, Brake Fluid, Automotive, dated 15 December 1964.
3. Military Specification, MIL-H-13910A, Hydraulic Fluid, Non-Petroleum Base, Automotive Brake, All-Weather, dated 15 May 1963.
4. Military Specification, MIL-P-46046A, Preservative Fluid, Automotive Brake System and Components, dated 26 August 1964.
5. Military Specification MIL-C-14055B, Cup, Hydraulic Brake Cylinder; Synthetic Rubber, dated 14 November 1961.
6. Society of Automotive Engineers Specification SAE J70b, dated December 1964.
7. Fischer, K., Angew. Chem 48, 394-6, (1935).

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APPENDIX A

TABLE I

BRAKE FLUID FROM MASTER CYLINDERS VEHICLES IN OPERATION AT A.P.G.

TMP No.	Vehicle	Date of Issue	Mileage	Type of Master Cylinder	Boiling Point	% Water
Military Vehicles With Diaphragms						
696	Ford Pickup	6/65	14	Large opening on firewall	390°F	0.56
574	Ford Pickup	6/65	8	Large opening on firewall	400°F	0.56
667	Ford Pickup	6/65	381	Large opening on firewall	394°F	0.64
663	Ford Pickup	1/65	3301	Large opening on firewall	381°F	1.52
678	Ford Pickup	6/65	4401	Large opening on firewall	347°F	1.41
845	I.H. Tractor	1/64	19567	Large opening on firewall	311°F	1.91
Military Vehicles Without Diaphragms						
429	Dodge Panel	9/56	39157	Large opening on firewall	320°F	0.76
230	Dodge Pickup	6/64	10133	Fluid taken from line	--	3.04
523	Dodge Sedan	3/64	11338	Large opening on firewall	291°F	2.08
760	Dodge Stake Platform	3/63	11999	Large opening on firewall	271°F	3.63
484	Dodge Bus	1/63	35251	Large opening on firewall	270°F	3.07
445	Dodge 3/4 ton	4/64	5254	Large opening on firewall	256°F	2.60
98	Dodge Pickup	6/64	14227	Large opening on firewall	381°F	1.66
307	Dodge 3/4 ton	8/64	11668	Large opening on firewall	300°F	2.18
265	Dodge Pickup	6/64	13404	Large opening on firewall	281°F	2.87
380	Chev. Pickup	8/58	72495	Small opening under floor	258°F	4.85
267	Chev. Pickup	5/57	31873	Small opening under floor	276°F	1.95
318	Chev. Pickup	7/57	73447	Small opening under floor	259°F	3.54
917	Chev. Pickup	7/57	41252	Small opening under floor	248°F	4.24
327	Chev. Pickup	12/56	64729	Small opening under floor	321°F	0.65

TABLE I (Cont'd.)

BRAKE FLUID FROM MASTER CYLINDERS VEHICLES IN OPERATION AT A.P.G.

TMP No.	Vehicle	Date of Issue	Mileage	Type of Master Cylinder	Boiling Point	% Water
Military Vehicles Without Diaphragms						
159	Chev. Pickup	12/56	54625	Small opening under floor	284°F	3.42
270	Chev. Pickup	6/57	57473	Small opening under floor	262°F	3.60
164	Chev. Pickup	7/57	77499	Small opening under floor	255°F	4.32
212	Ford Pickup	10/62	48064	Large opening on firewall	279°F	2.21
18	Ford Sedan	8/60	99170	Large opening on firewall	267°F	1.58
966	Ford Sedan	1/58	63071	Large opening on firewall	284°F	2.43
733	Ford Line Truck	1/62	11287	Large opening on firewall	268°F	3.06
751	Ford 2½	5/64	12005	Large opening on firewall	246°F	3.70
368	Ford Falcon	6/63	29748	Small opening under floor	270°F	3.30
729	GMC 2½ - 2x4	2/56	32237	Small opening under floor	266°F	4.40
710	GMC 2½	11/55	22962	Small opening under floor	308°F	1.20
790	GMC 2½	1/56	12745	Small opening under floor	291°F	1.59
895	Reo 2½	1/52	12850	Small opening under floor	300°F	1.12
953	Plymouth Sedan	3/63	5112	Large opening on firewall	282°F	2.26
16	Valiant Sedan	2/63	35840	Large opening on firewall	270°F	1.99
Civilian Vehicles						
1	Dodge Dart	1963	20000	Flat top - 3" filler	281°F	1.54
2	Chev. 4 dr.	1956	65000	Flat top - 1" filler	298°F	1.30
3	Cadillac 4 dr.	1964	28000	Dual with diaphragm	321°F	1.38
4	Lincoln 4 dr.	1961	7925 (since chg.)	Flat top 3" filler	317°F	1.19
5	Buick Wagon	1964	14500	3" filler w/diaphragm	330°F	1.10
6	Buick Special	1964	24000	3" filler w/diaphragm	305°F	1.21
7	Plymouth Wagon	1964	38000	3" filler - flat top	304°F	1.20
8	Chev. Wagon	1963	22000	Large - Thumb screw top	278°F	2.25
9	Renault	1962	1500 (since repair)	Glass reservoir	309°F	1.19

TABLE III

EFFECT OF WATER ON -40°F VISCOSITY OF BRAKE FLUIDS

Brake Fluid No.	Initial Values % Water	Initial Values -40°F Viscosity	2% Water Added Total % Water	2% Water Added -40°F Viscosity	After 7 days at 65% RH & 80°F Total % Water	After 7 days at 65% RH & 80°F -40°F Viscosity
1	.43	684.5	2.43	621.8	--	--
2	.24	912.3	2.24	1024.2	--	--
3	.19	1088.9	2.19	1193.0	6.57	1897.0
4	.38	1693	2.38	1363.7	--	--
5	.32	1660	2.32	1440.8	--	--
6	.19	1311.5	2.19	1479.3	--	--
7	.12	844	2.12	907.5	5.38	1470.0
8	.24	1113	2.24	1216.8	--	--
9	.31	1421	2.31	1554.6	6.30	2327.0
10	.41	622.0	2.41	705.7	--	--
11	.54	1578	2.54	1872.0	--	--
12	.24	1082.2	2.24	1126.8	6.39	1632.0
13	.23	198.9	2.23	257.7	6.23	395.8

Fluids 1 - 12 meet VV-B-680

Fluid 13 meets MIL-H-13910A

TABLE IV

EFFECT OF WATER ON FLASH POINTS OF BRAKE FLUIDS

Brake Fluid No.	Initial Flash Point °F*	Flash Point After Water Addition °F 2%	4%	6%
1	155	155	158	165
2	200	212	218	220
3	225	230	235	240
4	155	170	170	175

*Average of 3 determinations

Fluids 1,2,3 meet VV-B-680
Fluid 4 meets MIL-H-13910A

TABLE V

EFFECT OF WATER ON OXIDATION STABILITY
OF BRAKE FLUIDS - 10 DAYS, 158°F - WITH EXCESS BENZOYL PEROXIDE ADDED

Brake Fluid No.	Inspection: 0.5% Benzoyl Peroxide	Inspection: 0.5% Benzoyl Peroxide, 0.5% Water
1	Fail	Fail
2	Borderline	Fail
3	Pass	Borderline
4	Borderline	Fail
5	Pass	Borderline
6	Pass	Borderline
7	Pass	Borderline
8	Pass	Pass
9	Pass	Pass
10	Borderline	Borderline
11	Pass	Borderline
12	Pass	Borderline

All fluids under normal test conditions meet VV-B-680.

TABLE VI

EFFECT OF WATER CONTENT ON
RUBBER SWELLING AND SOFTENING

	Rubber Swelling (inches)		Rubber Softening (degrees)	
Fluid No.	w/o water	+5% water	w/o water	+5% water
1	0.026	0.012	7	5
2	0.025	0.012	8	7
3	0.036	0.013	9	6
4	0.031	0.014	9	5
5	0.034	0.017	9	7
6	0.025	0.014	7	6
7	0.037	0.022	9	7
8	0.014	0.007	4	3
9	0.031	0.016	9	5
10	0.028	0.016	9	7

All fluids meet VV-B-680.

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13 ABSTRACT

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Moisture produced the following effects - a. Boiling points are lowered in all brake fluids - drastically in so-called "high boiling" fluids. b. Flash points are increased. c. Cold temperature viscosities are usually increased. d. The stability of the brake fluid toward oxidation is decreased. e. Rubber swelling and softening is decreased.

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